

## **Molecular dynamics studies of interaction between hydrogen and carbon nano-carriers**

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### **ABSTRACT**

In this work, quantum molecular dynamics simulations (QMD) are performed to study the hydrogen molecules in three type of carbon nanostructures, C<sub>60</sub> fullerene, (5,5) carbon nanotube and graphene. Interactions between hydrogen and the nanostructures is of importance to understand hydrogen storage for the development of hydrogen economy. The QMD method overcomes the difficulties with empirical interatomic potentials to model the interaction among hydrogen and carbon atoms in the confined geometry. In QMD, the interatomic forces are calculated by solving the Schrodinger's equation with the density functional theory (DFT) formulation, and the positions of the atomic nucleus are calculated with the Newton's second law in accordance with the Born-Oppenheimer approximation. It is found that less than 58 hydrogen atoms can be stored in the C60 fullerene. With larger carbon fullerenes, more hydrogen may be stored. For hydrogen molecules passing through the fullerene, a particular orientation is required to obtain least energy barrier. For carbon nanotubes and graphene, physical adsorption may adhere hydrogen atoms to carbon atoms. In addition, hydrogen molecules can also be stored inside the nanotubes or between the adjacent layers in graphite, multi-layer graphene.

Keywords: Quantum molecular dynamics simulation, hydrogen, carbon, fullerene, nanotube, graphene

### **1. INTRODUCTION**

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The hydrogen storage problem is critical for the development of hydrogen economy (Strobel et al. 2006). In fact, the science about hydrogen, even though a very old subject, still requires detailed studies in terms of its behavior under high pressure (Labet et al. 2012). In addition to using metal hydrides, nano-cages provide an ideal solution to be a hydrogen carrier. Using carbon carriers for hydrogen storage has been studied by the *ab initio* simulation method (Dodziuki 2005, Ding et al. 2007, Pupysheva et al. 2008, Lin et al. 2008, Singh et al. 2009, Kruse et al. 2009), as well as experimental methods (Lachawiec et al. 2005, Lee and McKee 2008, Stadie et al. 2010). In addition to fullerenes, using carbon foam for storing hydrogen by physisorption and chemisorption is reported (Ding et al. 2007). For larger nanostructures, or called nanocages, molecules which are formed as a metal organic framework is an plausible candidate (Er et al. 2009). To improve the simulation accuracy, efforts have been placed to consider the non-covalent interaction in the hydrogen-carbon system (Kruse et al. 2009). By combining experimental and computational works, Miller et al. (2008) studied the hydrogenation problems on single-wall carbon nanotubes with polyamine reagents. In addition, Wu et al. (2010) experimentally demonstrated that through selective hydrogenation the cross-section of carbon nanotubes can be controlled. In addition to using carbon nanotubes for hydrogen storage, significant research has been performed to use the nanotubes as inclusions to enhance physical properties of materials (Li and Sun 2011).

In addition to pure carbon nanostructures, various nanostructures with other chemical elements and structures have been investigated, both computationally and experimentally. From the computational point of view, Averill et al. (2009) studied the hydrogenation problem on a single atomic layer of boron nitride and related chemical compound, inspired by the success of single layer graphene. Er et al. (2009) investigated the hydrogen storage problem with polyolithiated nanostructures. Similar systems have also been probed by Liu et al. (2009) for possible enhancement in hydrogen storage in Li-dispersed carbon nanotubes. Wang et al. (2009) calculated the problem with hydrogen in Ca-coated fullerenes. In addition, Salam et al. (2013) studied the hydrogen adsorption problem on mixed oxides, and Mattesini et al. (2006) investigated the mechanical and spectroscopy properties of a metal-organic framework (MOF), which is a potential candidate for high-capacity hydrogen storage. Experimentally, Li and Yang (2006) have demonstrated that hydrogen storage on MOF's can be achieved by the spillover method.

Molecular dynamics (MD) simulation is an important tool to study nanoscale systems that are experimentally inaccessible, and details of the simulation principles and techniques can be found in Tuckerman's book (2010). Recently interactions between aluminum solute atoms and dislocations in magnesium alloys have been studied by the MD simulation (Shen 2013). However, conventional MD simulation relies on empirical interatomic potentials to describe interactions among atoms. The potentials are, in general, fitted with experimental data to determine the necessary parameters in the potential functions. There are two drawbacks in the conventional MD. One is the choice of the potential functional and the other the determined parameters are only valid for bulk materials since they are fitted with experimental data from bulk materials. Use of quantum molecular dynamics (QMD) simulation bypasses the drawbacks since the interatomic force is calculated from the electron interaction, but

severely increases computation cost. There are numerous strategies to implement QMD simulation, and in this work the SIESTA code is adopted to simulate hydrogen-carbon systems (Soler et al. 2002).

The present studies focus on the interaction between hydrogen and the following three carbon nanostructures: C<sub>60</sub> carbon fullerene, (5,5) carbon nanotubes and graphene. In this work, the C<sub>60</sub> fullerene is studied at room temperature under high pressure to understand its stability. Then, various number of hydrogen atoms is embedded into the fullerene to investigate the stability of the hydrogen-carbon systems. To study the filling mechanism, hydrogen atoms are placed at outside the fullerene under 10 GPa pressure, and it is observed that hydrogen atoms may diffuse into the fullerene.

## 2. QUANTUM MOLECULAR DYNAMICS SIMULATION

The general description of the governing equation in quantum molecular dynamics is described in Section 2.1, the density function theory in Section 2.2, and the numerical implementation of the SIESTA software package in Section 2.3.

### 2.1 The Schrödinger equation

Physical properties of materials at the nano-scales are ultimately determined by their electronic structures and interactions, which are governed by the time-independent Schrödinger equation, as shown in Eqs. (1) and (2). The electron wave function  $\Psi = \Psi(x_1, x_2, x_3)$  is governed by the eigenvalue problem with the total energy  $E$  as the eigenvalue of the state.

$$H\Psi = E\Psi \quad (1)$$

$$\hat{H} = \sum_i -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \sum_l \frac{-Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} \quad (2)$$

The first term is the kinetic operator, involving the Laplacian differential operator, for the number of electrons  $N$ . The second term describes the electron-nucleus interactions, the third term for the electron-electron interactions and the last term the nucleus-nucleus interactions. It is noted that the Hamiltonian differential operator  $H$  is position-dependent. Position vectors  $\mathbf{r}$  and  $\mathbf{R}$  delineate the location of electron and nucleus, respectively. The symbol  $Z$  indicates the nucleus charge, and subscripts  $i$  and  $k$  label the electrons and nuclei, respectively. The number of nucleus is assumed to be  $M$ . The Born-Oppenheimer approximation is embedded in the Eq. (1) to simply the many-body Hamiltonian by using the large mismatch between electron and nucleus mass

## 2.2 Density functional theory

Solving the Schrodinger's equation many-electron systems is not practicable. From the viewpoint of variational calculus, the quantum system must satisfy the following variational condition.

$$\delta[\langle\Psi|\hat{H}|\Psi\rangle-E\langle\Psi|\Psi\rangle]=0 \quad (3)$$

Here  $E$  is the lagrangian multiplier, and its physical meaning is the total energy of the system, and Hamiltonian operator  $\hat{H}$  a partial differential operator, containing kinetic and potential operators. The analytical solution of the above variational problem leads to the following partial differential equation.

$$\hat{H}\Psi = E\Psi \quad (4)$$

The solution of the above eigenvalue problem yields the energy ( $E$ ), as the eigenvalue, that is required for ground or excited states, and corresponding wave functions ( ). In computation, periodic boundary conditions are adopted for simulate infinite systems, and hence an energy cutoff is introduced for computation efficiency. Mathematically, this cutoff sets how many terms would be included in the fourier series, i.e. superposition of plane waves.

## 3.2 SIESTA software package

The exact solution of the Schrödinger equation for the many-body problem are unattainable, and hence the density functional theory (DFT) is introduced to solve the Schrödinger equation as a variational problem numerically. In this work, the software package SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is adopted to calculate the hydrogen-carbon systems (Soler et al. 2002). The positions of the hydrogen atoms are first manually placed inside the carbon nanocages. The conjugate gradient (CG) method, then, is adopted to find a minimal energy state, which dictates the residual forces smaller than 0.1 eV/Å. After the CG, quantum molecular dynamics simulation is performed to study the stability of the systems.

The SIESTA program uses the self-consistent algorithm to solve the one-particle Kohn-Sham (KS) Schrodinger-like equation, and finds the eigenvectors (wave function) and eigenvalues (energy) of the systems. The solution technique is based on the expansion of wave functions using localized, numerical orbitals as basis sets. In this work, the diagonal method for the numerical scheme in SIESTA was adopted. The solution technique is based on the expansion of wave functions using localized, numerical orbitals as basis sets of finite range. Furthermore, norm-conserving Troullier-Martines pseudo potentials in the Kleinman-Bylander factorized form and a double-basis set. The generalized gradient approximation for the exchange-correlation potential was implemented.

### 3. RESULTS AND DISCUSSION

In this section, the hydrogen and fullerene system is reported first. Then, the hydrogen and carbon nanotube system is discussed in Section 3.2. Finally, the interaction between hydrogen and graphene is discussed in Section 3.3.

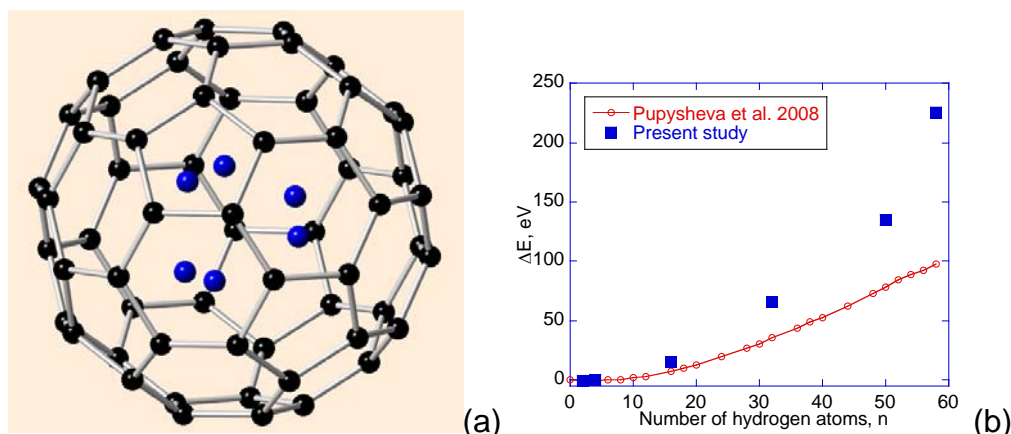


Figure 1. (a) The  $H_6@C_{60}$  molecular dynamics model, and (b) formation energy versus the number of hydrogen atoms.

#### 3.1 The hydrogen and $C_{60}$ fullerene system

It is well known that  $C_{60}$  fullerene is one of the most stable chemical compounds. By introducing hydrogen into the fullerene, denoted as the  $H_n@C_{60}$  chemical compound, one may utilize the fullerene as a hydrogen carrier. Figure 1 (a) shows the six hydrogen atoms (i.e.  $H_6@C_{60}$ ) form 3  $H_2$  hydrogen molecules by the quantum molecular dynamics, after equilibration. However, it is noted that with large amount of hydrogen atoms inside the fullerene, it is likely to form bonding between the hydrogen and carbon atoms. In addition, the pressure inside the fullerene drastically increases with the number of hydrogen atoms, as discussed in Pupysheva et al. (2009). With this large increase in pressure, the work by Labet et al. (2012) is crucial to understand the nature of hydrogen bond under high pressure. Through our quantum molecular dynamics simulations, Figure 1 (b) shows the formation energy,  $E_f$ , as calculated by Eq. (8) below, increases with the number of hydrogen atoms.

$$E_f = E(H_n @ C_{60}) - E(C_{60}) - \frac{n}{2} E(H_2) \quad (5)$$

The formation energy calculated in this work is consistent with that reported by Pupysheva et al. (2009), but slightly larger. Since both of our models show the breakage of the fullerene with 58 hydrogen atoms inside, the difference in the calculated formation energy may be due to the size of energy cutoff. At  $n = 58$ , the

difference in the formation energy is larger than other  $n$  values, since the breakage of fullerene may lead to additional amount of errors in the calculation.

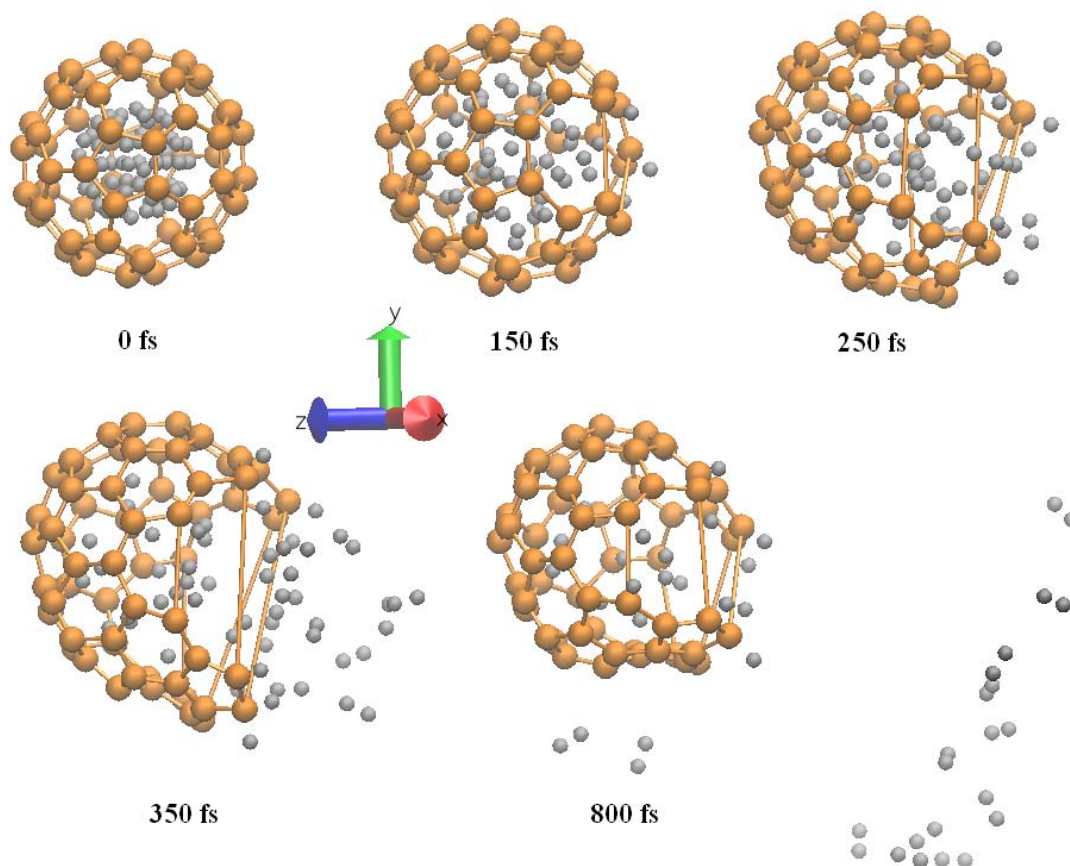


Figure 2. Time evolution of the  $H_{58}@C_{60}$  model to show the breakage of the fullerene cage.

Figure 2 shows the breakage of the fullerene with  $n = 58$  due to exceptional large pressure generated by the hydrogen. At 150 femto seconds (fs), some of the hydrogen escapes from the fullerene, and then at 250 fs the  $C_{60}$  opens with large amount of hydrogen moving outwards. Between 350 and 800 fs it can be seen that the fullerene becomes smaller, and appears to recover its original shape. The unrealistically longer carbon-carbon bonds, as shown in yellow color, indicate the original connection between the two carbon atoms.

In order to test the energy penalty for a hydrogen molecule passing through the fullerene from outside to inside without breaking the  $C_{60}$ , Figures 3 (a) and (b) show the two arrangements of the hydrogen molecule, called the horizontal and vertical, respectively. The color in (a) and (b) indicate the valence pseudocharge density, and the difference between valence pseudocharge density and sum of atomic valence pseudocharge density, defined by

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_a(\mathbf{r}). \quad (6)$$

The pseudocharge density describe the electronic structures of the atoms in the system. As can be seen in Figure 3 (c), the energy barrier for the horizontal case is much larger than that of the vertical case. Therefore, without breaking the fullerene, we propose that the refilling and release mechanism of hydrogen in fullerene should involve the orientation of the hydrogen molecules to reach a position with least energy barrier. The results of Figure 3 were obtained by manually place the hydrogen molecules in the desired position around the fullerene, and then calculated with equilibration quantum molecular dynamics simulation.

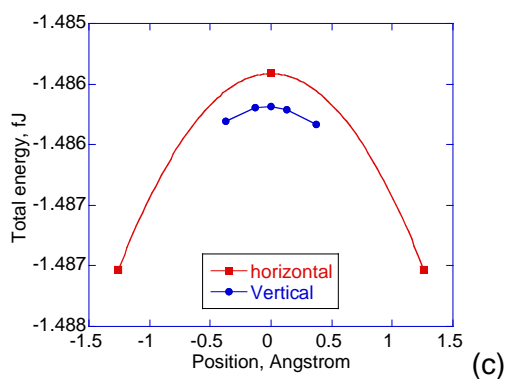
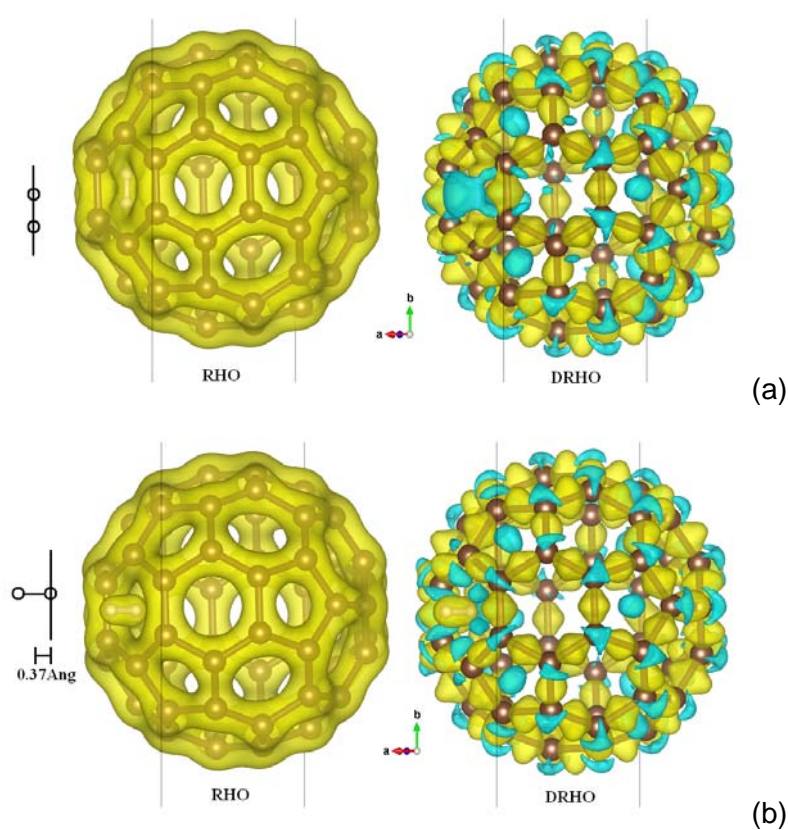


Figure 3. (a) The horizontal configuration of the hydrogen molecule being placed on the wall of the fullerene, (b) the vertical configuration of the hydrogen molecule being placed in touch of the wall of the fullerene, and (c) the ground-state energy of the hydrogen-fullerene system versus various locations of the hydrogen molecule.

To further test the vertical arrangements of hydrogen molecules on the fullerene, we placed hydrogen molecules on all the hexagonal ring on the fullerene, and perform QMD simulation on the system. Results are shown in Figure 4, and it can be seen that, after equilibration, most of the hydrogen atoms are trapped inside the fullerene and some of them escaped away. It is known that for large amount of hydrogen atoms inside the fullerene, in addition to the form of hydrogen molecules, hydrogen atoms may also be attached to a carbon atom by physisorption.

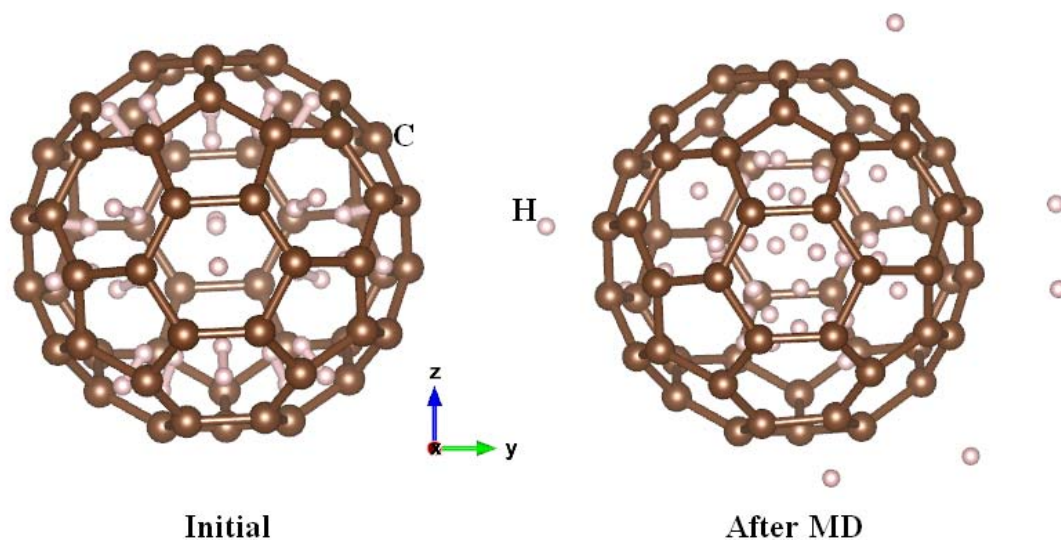


Figure 4. The initial and final configuration of the hydrogen-fullerene system.

### 3.2 The hydrogen and (5,5) carbon nanotube system

Carbon nanotubes have long to thought to be used as a hydrogen storage device. Figures 5 (a) and (b) show the physisorption of hydrogen atoms on the outside of the (5,5) carbon nanotubes for one and seven hydrogen atoms, respectively. It can be seen that for one hydrogen atom, the physisorption is strong enough to deform the carbon nanotube. It is expected to observe that more hydrogen atoms being adsorbed on the outside of the nanotubes. However, as shown in Figure 5 (b), it is possible for the hydrogen to form  $H_2$  molecules, and escape from the weak field generated by physisorption between the hydrogen and carbon atoms. The rational for this particular case is the initial configuration to associate two hydrogen atoms with a carbon ring, hence the competition between the two hydrogen atoms to fight for a carbon ring causes both of the hydrogen atoms cannot physically adsorb on the ring, and form a



neutral hydrogen molecule. Once the hydrogen molecule is formed, the interaction between the molecule and nanotubes relies on the van der Waal type weak force. Therefore, the hydrogen molecule may not stay near the nanotube.

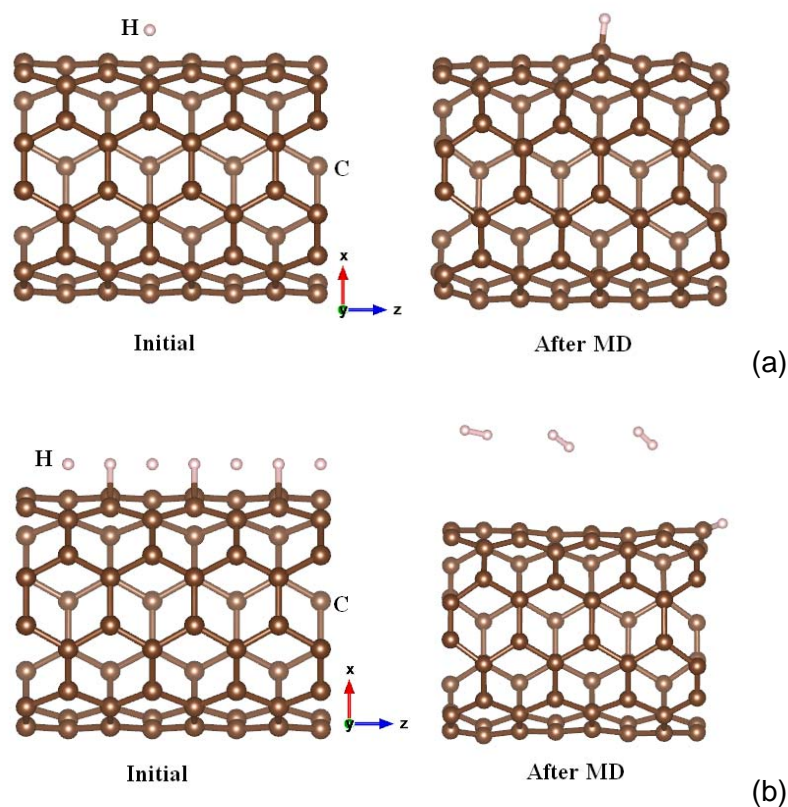


Figure 5. (a) An hydrogen atom physically adsorbed on the outside of the (5,5) carbon nanotube, and (b) interaction between seven hydrogen atoms and the (5,5) nanotubes.

It is remarked that the local curvature of the nanotube introduces a fractional  $sp^3$  bond character on the top of the dominate  $sp^2$  bond, which makes the nanotubes behave differently from graphene, as discussed in the next section. Smaller tubes have stronger  $sp^3$  characteristics, and hence more deviations from graphene. In addition to physisorption, there are different ways to utilize nanotubes to store hydrogen. For example, one can use the nanotubes similar to the fullerene, and store the hydrogen inside the tubes, which require further studies to show its performance as a hydrogen carrier.

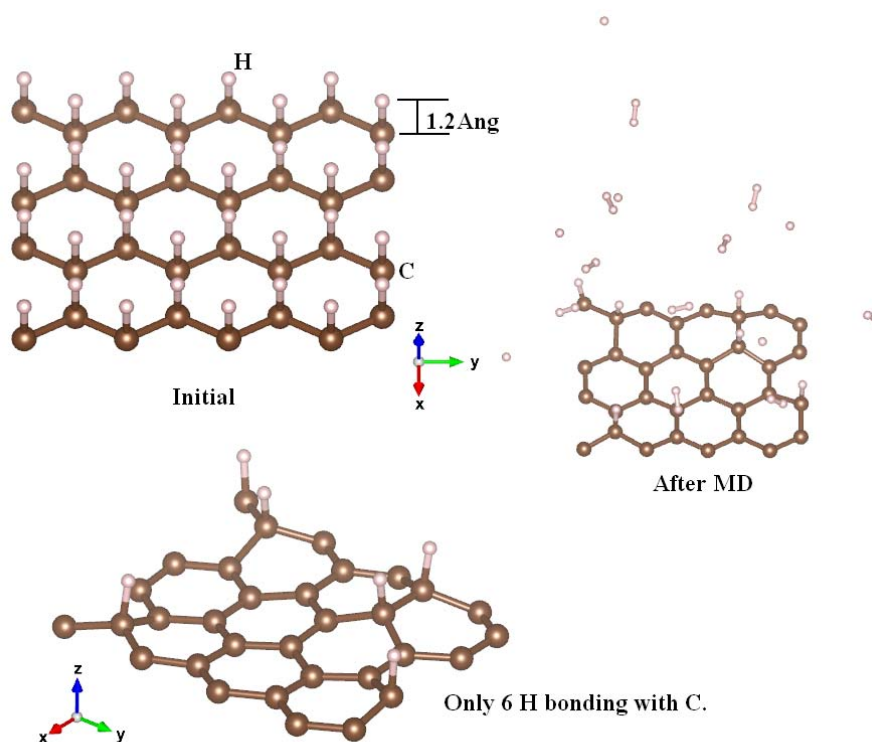


Fig.6 Comparison of formation energy for various number of hydrogen atoms in the  $C_{60}$  fullerene. Only six hydrogen atoms bonded with the graphene by physisorption.

### 3.3 The hydrogen and graphene system

To test the fully hydrogenation on the single-layer graphene, Figure 6 shows that, after equilibration simulation with the NVT at 300 K, six out of 24 hydrogen atoms remain physically adsorb on the graphene. Other hydrogen atoms move away from graphene, and some of them form hydrogen molecule. Furthermore, after equilibration, the graphene may no longer stay in a plane, and become H-induced corrugated configuration, as seen in the bottom figure in Figure 6.

It is known that spillover or other mechanism is required to separate the hydrogen molecule into two hydrogen atoms for them being physically adsorbed on graphene, as discussed in Figure 6. However, without catalyst effects on hydrogen separation, it is entirely possible for hydrogen molecules being stored in multilayered graphene. Figure 7 demonstrates this idea by using the three-layer graphene with six hydrogen molecules initially placed between the layers. In Figure 7 (a) the simulation temperature was 300 K, and in (b) the temperature was 500 K. Both of the top view and side view are plotted. It can be seen that, regardless of temperature, the hydrogen molecules remain as the H<sub>2</sub> form, and are trapped in the graphene layers. This results may shed light on using graphite to store hydrogen molecules, instead of the atomic form of hydrogen through physisorption or chemisorption. Refilling and extraction

mechanisms of hydrogen into and out of the graphite require further computational and experimental studies.

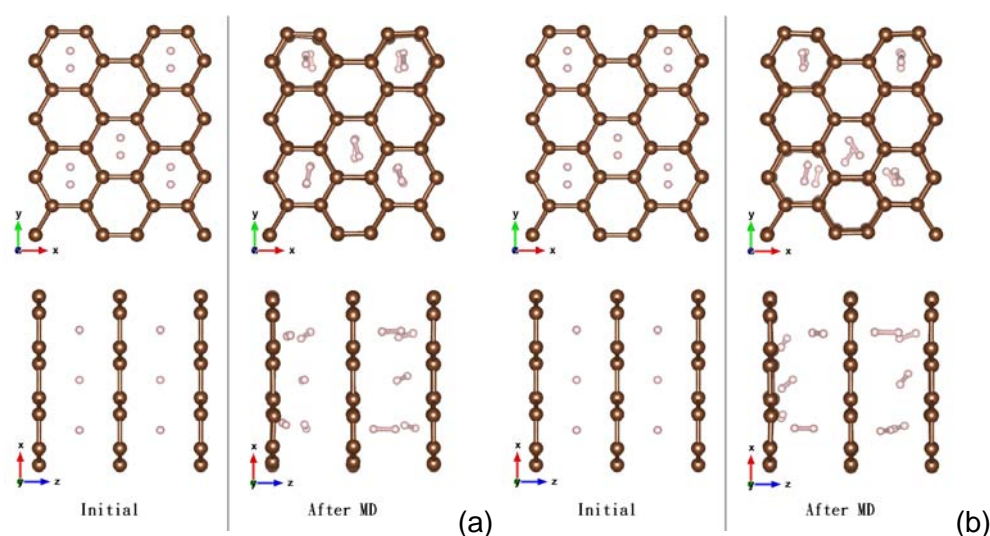


Figure 7. Hydrogen molecules in the three-layer graphene nanostructure at (a) 300 K and (b) 500 K.

#### 4. CONCLUSIONS

In this work, the interactions between hydrogen and the C60 fullerene, (5,5) carbon nanotubes, as well as single-layer and multi-layer graphene, have been studied with the quantum molecular dynamics simulation. Significant amount of the hydrogen may be stored in fullerene, depending on the size. Inside the fullerene, the bonding nature of the hydrogen is complex due to high pressure for large  $n$ . For small  $n$ , the hydrogen atoms may form hydrogen molecules or single atomic form being adsorbed to a carbon atom. However, with pressure built up in the fullerene for a large amount of hydrogen, breakage of the fullerene is inevitable. For hydrogen molecules passing through the fullerene, a particular orientation is required to obtain least energy barrier. Detailed refilling and release mechanisms for hydrogen in fullerene require further studies. Carbon nanotubes may also physically adsorb the hydrogen atoms on the surface, or store them inside the tubes. From the hydrogen-graphene systems, adsorption of hydrogen on carbon atoms can be achieved. Once hydrogen is adsorbed, the graphene cannot maintain its two-dimensional feature. In addition, the hydrogen molecules may be stored in multi-layer graphene.

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